



# The mechanism of the CH<sub>4</sub>/O<sub>2</sub> reaction on the Pd–Pt/γ-Al<sub>2</sub>O<sub>3</sub> catalyst: A SSITKA study



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## ABSTRACT

This work is mainly dedicated to the studies of the reaction mechanism of complete methane oxidation on the γ-alumina palladium–platinum catalyst by means of the steady state isotopic transient kinetic analysis (SSITKA) with <sup>12</sup>CH<sub>4</sub>/<sup>13</sup>CH<sub>4</sub> and <sup>16</sup>O<sub>2</sub>/<sup>18</sup>O<sub>2</sub> switches. Such kinetic parameters as the average surface life-time and the surface concentration of methane, oxygen, carbon dioxide and intermediates leading to its formation were determined. It was found that carbon dioxide is formed with two different rates. The average surface life-time of fast formed carbon dioxide change from 11.2 s at 637 K to 0.2–0.3 s at higher temperatures, while the surface concentration of fast formed carbon dioxide and intermediates leading to it change from 3.1 μmol/g at 637 K to 1.8 μmol/g at 980 K. Carbon dioxide formed with a slow rate is present on the catalyst surface only above 637 K. At higher temperatures the values of its average surface life-time are close to 1.7–1.8 s, while the surface concentration of slow formed carbon dioxide and intermediates leading to it change from 14.8 μmol/g at 755 K to 16.3 μmol/g at 980 K. The coverage of the surface of the palladium–platinum active phase with fast formed carbon dioxide and intermediates leading to it is in the order of 0.16–0.17 in the range of 673–755 K and 0.125 – at 980 K. Much more higher is the surface coverage with slow formed carbon dioxide – 0.8 and 0.92 at 755 K and 980 K, respectively. It was also found that oxygen from the crystal lattice of the catalyst takes part in oxidation of methane, as well as that oxygen atoms are exchanged between the gas phase and the crystal lattice of the catalyst. The very long live-time of oxygen leading to formation of carbon dioxide, in the order of 80–380 s, and very large formal coverage of the surface of palladium–platinum active phase with oxygen desorbed to the gas phase and oxygen leading to formation of carbon dioxide, scores of times exceeding the formal monolayer, clearly prove that a very large pool of subsurface oxygen participates in methane oxidation. It was also found that only at the lowest temperature of the reaction small amount of reversibly adsorbed methane resists with a very short life-time on the catalyst surface. It may be concluded that two different kinds of active centres (α—more active, but less numerous and β—less active, but more numerous) exist on the “working” surface of the catalyst and the process of methane oxidation proceeds simultaneously according to two different reaction mechanisms (Mars–van Krevelen and Langmuir–Hinshelwood). The extent of their participation in oxidation of methane is different and depends on the reaction temperature. Moreover, the process of methane oxidation proceeds not only simultaneously according to two different mechanism of the reaction, but also with different rates determined by the kind of active centres.

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## 1. Introduction

Complete oxidation (flameless combustion) of methane is one of catalytic processes, which can considerably impact on the emission decrease of impurities (NO<sub>x</sub>, CO and hydrocarbons) into the earth atmosphere. The replacing of flame combustion of natural

gas by flameless combustion is very desirable, but the cost of a new technology and the uncertainty of economic benefits inhibited the development of this technological solution. However, the catalytic combustion has also others important applications, such as removing (oxidation) of methane from post-ventilation air of coal mines. Methane is a greenhouse gas much more harmful than carbon dioxide, because it absorbs 21-times more infrared radiation [1]. Moreover, methane is one of the most important energetic and chemical raw material, of which, the demand continuously increases. Thus, reduction of methane emission into atmosphere

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$\alpha$	active centres on the catalyst surface (more reactive, but less numerous than $\beta$ )
$\beta$	active centres on the catalyst surface (less reactive, but more numerous than $\alpha$ )
BET method	Brunauer Emmett Teller method
$\delta$	specific weight of Pd and Pt
$D_i$	average diameter of metal crystallites in each diameter range
DRIFTS	diffuse reflectance infrared Fourier transform spectroscopy
EDS	energy dispersive X-ray spectroscopy
GHSV	gas hourly space velocity
$N_i$	numbers of metal crystallites in a specific size range
$S_{H_2}$	surface of 1 g of both metals (Pd and Pt)
SSITKA	steady state isotopic transient kinetic analysis
STEM	scanning transmission electron microscopy
XRF	X-ray fluorescence spectroscopy

with the simultaneous rise of possibilities of methane obtaining from additional sources should be one of the major aims of scientific and industrial actions.

In the group of catalytic materials demonstrating the best properties in the process of complete methane oxidation, supported palladium and platinum catalysts are very often itemised [2–7]. They have the highest activity, one hundred percent selectivity into carbon dioxide and water vapour, as well as acceptable thermo-stability, obviously dependent on the kind of a support. An interesting solution, which has also received much attention [8–13], are palladium–platinum catalysts. These bimetallic catalysts present better stability of their activity in the process of complete methane oxidation, and furthermore, the most of them are more active than monometallic catalysts [9–13]. Therefore, this combination of components is more and more frequently studied by scientists and proposed as the alternative to monometallic palladium or platinum catalysts. However, there are still many controversial and unresolved issues concerning the course of the reaction of complete methane oxidation on palladium–platinum catalysts. The most important are questions of what is kind of a mechanism and what is a reaction pathway. They are very difficult issues to solve, especially when we take into account a lot of contradictory opinions concerning similar problem about the reaction mechanism of complete methane oxidation on palladium catalysts. For which, two completely different catalytic mechanisms of methane oxidation are often proposed [14–17].

In order to supply new information, which enable us to better understood the process of the complete methane oxidation on palladium–platinum catalysts the studies with application of the steady state isotopic transient kinetic analysis (SSITKA) were carried out. The basic advantage of this technique is the possibility of investigation of the catalytic process in real time and conditions on the surface of “working” catalysts. Therefore, the SSITKA method enables us to provide many unique and thereby valuable experimental data concerning, among others, the reaction pathway and the mechanism and also such kinetic parameters as: the average surface life-time and the surface concentration of reaction intermediates [18,19]. For palladium catalysts, the values of the average surface life-time and the surface concentration of oxygen, methane and carbon dioxide and the methane oxidation intermediates leading to formation of carbon dioxide were estimated in our earlier studies [7,20–22]. Moreover, such important information as participation of oxygen from the catalyst lattice in the process of methane oxidation, which suggested that this reaction proceeds, at least partially, according to the Mars–van Krevelen mechanism as well as

dependence of the number of active sites on the reaction conditions were indicated. It was also suggested that methane molecules can be reversible adsorbed on the palladium catalyst and that oxygen ions from the lattice of the palladium catalyst can be exchanged with oxygen from the gas phase. As they were very informative studies, the SSITKA method was also applied here for analysis of methane oxidation over bimetallic Pd–Pt/Al<sub>2</sub>O<sub>3</sub> catalyst “working” at the steady-state of the process, using both <sup>12</sup>CH<sub>4</sub>/<sup>13</sup>CH<sub>4</sub> and <sup>16</sup>O<sub>2</sub>/<sup>18</sup>O<sub>2</sub> isotope-labelled reactant switches at the same reaction conditions and with the same catalyst. It should be emphasized that results of such studies over bimetallic catalyst are presented for the first time in this paper. We should note at this point that correct and precise analysis of SSITKA results is a big challenge. It requires considering a number of important factors—precisely described in review papers [18,19]. In the case of studies of the complete catalytic oxidation of methane, the readsorption of CO<sub>2</sub> can be one of the more important factors, especially when we compare this process with the water gas shift reaction, where the readsorption of CO<sub>2</sub> was observed, among others, by Kalamaras et al. [23–25].

## 2. Experimental

### 2.1. Catalyst preparation

The palladium–platinum catalyst was prepared by the ion exchange of the commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support (Engelhard Al-0104) with the aqueous solution (pH 10) of Pd(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> and Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>. The precursor was dried at 383 K (2 h) and calcined at 773 K (1 h). Prior to almost all experiments (exception is the BET analysis) a catalyst sample was reduced with hydrogen at 573 K (1 h).

### 2.2. Methane oxidation

The activity of the palladium–platinum catalyst was tested in a fixed-bed quartz reactor placed inside an electric furnace with the system enabling the monitoring and controlling the temperature. The load weight of a catalyst bed was 0.1 g. The reaction mixture contained 2 vol.% of methane, 6 vol.% of oxygen and inert gases (helium and argon). The total volumetric flow rate of the reaction mixture through the catalytic bed was 100 cm<sup>3</sup>/min, resulting in a GHSV of about 48,000 h<sup>−1</sup>. The temperature of the catalyst was increased at the rate of 10 K/min. The composition of the post-reaction mixture was analysed by the quadruple mass spectrometer (Hiden HPR 20 QIC).

### 2.3. Catalyst characterization

The palladium and platinum contents in the catalyst were determined by the X-ray fluorescence (XRF) method. The measurements were performed by the energy-dispersive XRF spectrometer (Canberra 1510) equipped with the liquid nitrogen-cooled Si(Li) detector.

The total BET surface area of the reduced catalyst was measured by the low-temperature (77 K) nitrogen adsorption in the ASAP 2405N v1.0 analyser (Micromeritics), assuming that one nitrogen molecule occupies the area of 0.162 nm<sup>2</sup>.

The amount of surface metal atoms and mean size of metal crystallites were determined on the basis of the hydrogen chemisorption, assuming that one hydrogen atom is adsorbed on the area occupied by one surface metal atom and the surface area occupied by one atom of hydrogen equals to 0.065 nm<sup>2</sup>. The chemisorption experiment was carried out in the Autosorb-1-C analyser (Quantachrome) on the catalyst reduced at the

temperature of 383 K. The average size of metal crystallites ( $d$ ) was calculated assuming their spherical shape from the equation:

$$d = \frac{6}{S_{H_2} \delta} \quad (1)$$

where  $S_{H_2}$  is the surface of 1 g of both metals (Pd and Pt),  $\delta$  is the specific weight of Pd and Pt.

The composition and surface morphology of the catalyst was studied by the high resolution transmission electron microscope FEI Titan<sup>3</sup> Cube 60–300 working in the scanning transmission mode (STEM) coupled with energy dispersive X-ray spectroscopy (EDS). Prior to the microscope analysis the reduced sample of the catalyst was powdered and suspended in ethanol and then obtained suspension was placed on the standard Cu grid and left in air at room temperature until solvent evaporated completely. After the microscope analysis, from the STEM images, 52 metal crystallites were picked up and the sizes of them were determined as the average of two diameters of each crystallite. The average size of metal crystallites was calculated ( $d$ ) from the equation:

$$d = \frac{\sum N_i D_i}{\sum N_i} \quad (2)$$

where  $N_i$  is the numbers of metal crystallites in a specific size range,  $D_i$  is the average diameter of metal crystallites in each diameter range.

#### 2.4. SSITKA experiment

The SSITKA studies were conducted in the fixed-bed quartz reactor filled with 0.1 g of the catalyst sample at temperatures 637, 755 and 980 K providing low, medium and high conversion of methane. When the steady state of the catalytic reaction was obtained at the each required temperature, the switching between the mixture containing 2 vol.% of  $^{12}\text{CH}_4$ , 6 vol.% of  $\text{O}_2$ , 10 vol.% of Ar and 82 vol.% of He and the mixture containing 2 vol.% of  $^{13}\text{CH}_4$ , 6 vol.% of  $\text{O}_2$ , 10 vol.% of Kr and 82 vol.% of He or between similar mixtures containing normal methane but different oxygen isotopes ( $^{16}\text{O}_2$  and  $^{18}\text{O}_2$ ) was carried out. Before all SSITKA experiments the steady state of the reaction of complete methane oxidation was maintained by minimum 2 h. There was no catalyst deactivation observed even for much longer period of time-on-stream; the conversion of methane was stable on the level characteristic of applied reaction conditions: real concentrations of the products, i.e. carbon dioxide and water vapour, constant amounts of the heat released during this exothermic reaction and constant reaction temperature as well as invariable another reaction parameters. The total flow rate of the reaction mixture through the catalyst bed was  $100 \text{ cm}^3/\text{min}$ , resulting in a GHSV of about  $48,000 \text{ h}^{-1}$ . The composition of the post-reaction mixture was analysed by the quadrupole mass spectrometer (Hiden HPR 20 QIC) with a sampling rate of 5 analyzes/s. After each SSITKA experiment to determine the concentration of methane, oxygen and carbon dioxide in the post-reaction mixture, the analysis of the template mixture was carried out.

The obtained data directly from the mass spectrometer were subjected to the mathematical analysis, which consisted of several stages. First, the base line, i.e. the level of the apparatus noise was subtracted from obtained results. Then, all values of analytical signals important from the point of view of SSITKA studies were normalized (divided by the maximum values for methane, oxygen, carbon dioxide or inert gas). This operation was performed for the following signals of the mass spectrometer:  $m/z = 15, 17, 32, 34, 36, 40, 44, 45, 46, 48$  and 84 characteristic, respectively, for  $^{12}\text{CH}_4$ ,  $^{13}\text{CH}_4$ ,  $^{16}\text{O}_2$ ,  $^{16}\text{O}^{18}\text{O}$ ,  $^{18}\text{O}_2$ , Ar,  $\text{C}^{16}\text{O}_2$  ( $^{12}\text{CO}_2$ ),  $^{13}\text{CO}_2$ ,  $\text{C}^{16}\text{O}^{18}\text{O}$ ,  $\text{C}^{18}\text{O}_2$  and Kr. To prove better visualization of the obtained results the measurement points were smoothed in OriginPro 8 software using the adjacent averaging algorithm. Subsequently, on the basis

of delays between argon (krypton) and  $^{12}\text{CH}_4$ ,  $^{16}\text{O}_2$ ,  $^{12}\text{CO}_2$ ,  $\text{C}^{16}\text{O}_2$  ( $^{13}\text{CH}_4$ ,  $^{18}\text{O}_2$ ,  $^{13}\text{CO}_2$ ,  $\text{C}^{18}\text{O}_2$ ) and the area under the peak of  $^{16}\text{O}^{18}\text{O}$  and  $\text{C}^{16}\text{O}^{18}\text{O}$  the values of the average surface life-time of methane, oxygen, carbon dioxide and the methane oxidation intermediates leading to formation of carbon dioxide were determined. For this mathematical analysis, MS Excel software for subtraction of the signal corresponding to Ar from the signals corresponding  $^{12}\text{CH}_4$ ,  $^{16}\text{O}_2$ ,  $^{12}\text{CO}_2$  and  $\text{C}^{16}\text{O}_2$ , while PeakFit software for calculation of area under the peak of  $^{16}\text{O}^{18}\text{O}$  and  $\text{C}^{16}\text{O}^{18}\text{O}$  as well as under the peaks obtained from substitution of Ar from  $^{12}\text{CH}_4$ ,  $^{16}\text{O}_2$ ,  $^{12}\text{CO}_2$  and  $\text{C}^{16}\text{O}_2$  were used. Based on the values of the average surface life-time, taking account of the composition of the reaction mixture (2 vol.% of  $^{12}\text{CH}_4$  and 6 vol.% of  $\text{O}_2$ ), its total flow rate ( $100 \text{ cm}^3/\text{min}$ ), the conversion of methane and the weight of the catalyst bed (0.1 g), the surface concentration of methane, oxygen, carbon dioxide and the methane oxidation intermediates leading to formation of carbon dioxide were determined. The calculated values of the surface concentration were expressed in micromoles per 1 g of the catalysts ( $\mu\text{mol/g}$ ). Some additional information about the measurement procedure and data treatment can be found in the paper [20], as well as in the review papers [18,19] concerning theoretical and practical aspects of the SSITKA analysis. One of the most important things which should be more widely mentioned is the analysis of the delay between Ar and  $^{12}\text{CO}_2$ . After subtracting the values corresponding to Ar from the normalized concentration of  $^{12}\text{CO}_2$ , the Extreme Value 4 Parameter Tailed (Amplitude) algorithm was fitted in the obtained data and on the basis of it, the surface area was determined.

It should be noted that some values of the average surface life-time and surface concentration obtained for high conversion of methane can be overestimated due to mass transfer limitations. At high conversion of methane they are really integral of values characteristic of those for a range of partial pressures of methane and oxygen (as the oxidation of methane is the first order reaction with respect to the latter reactant its small pressure change is less important) prevailing in the catalyst bed, which is a small one, ca. 2 mm in height). Nonetheless, also these parameters are necessary for better understanding of the process of complete methane oxidation on the Pd–Pt/ $\text{Al}_2\text{O}_3$  catalyst, especially its mechanism, as well as such decision resulted from the experimental difficulties in the accurate estimation of these values, when the concentration of  $\text{CO}_2$  was low.

The data for the logarithmic analysis of the effects of the switching between the mixture containing  $^{12}\text{CH}_4$ ,  $\text{O}_2$ , Ar, He and the mixture containing  $^{13}\text{CH}_4$ ,  $\text{O}_2$ , Kr, He, as well as between the mixture containing  $^{16}\text{O}_2$ ,  $\text{CH}_4$ , Ar, He and the mixture containing  $^{18}\text{O}_2$ ,  $\text{CH}_4$ , Kr, He included in this paper were prepared in the following steps:

- the value of time for argon was subtracted from the value of time for  $^{12}\text{CO}_2$  and  $\text{C}^{16}\text{O}_2$ , at the same values of the normalized concentration of Ar and  $^{12}\text{CO}_2$  as well as Ar and  $\text{C}^{16}\text{O}_2$ ;
- the natural logarithm of the corrected values of the normalized concentration of  $^{12}\text{CO}_2$  and  $\text{C}^{16}\text{O}_2$  was determined.

### 3. Results and discussion

#### 3.1. Catalyst physicochemical properties

The Pd–Pt/ $\text{Al}_2\text{O}_3$  catalyst contains 0.147 wt.% of palladium and 0.090 wt.% of platinum. Its total BET surface area is  $101.2 \text{ m}^2/\text{g}$ . From chemisorption measurement the amount of surface metal atoms was found to be  $18.24 \mu\text{mol/g}_{\text{cat}}$ . The mean size of metal crystallites determined by using the chemisorption method is 1.1 nm. The fact, that the metals are strongly dispersed on the support surface

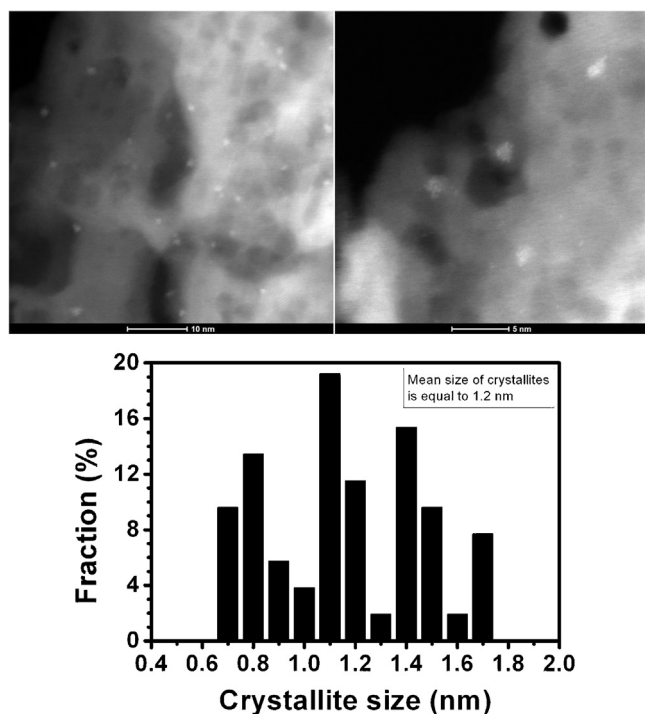


Fig. 1. STEM images of the reduced palladium–platinum catalyst and the size distribution of active phase crystallites.

is confirmed by the STEM analysis (Fig. 1). The mean size of metal crystallites (1.2 nm) calculated on the basis of the STEM image is almost the same like obtained by the chemisorption method. The EDS analysis of dozen or so active phase crystallites (six of them is shown in Fig. 2) proves existence of the pure palladium phase and the palladium–platinum phase (alloy between Pd and Pt). Such composition of the active phase of Pd–Pt/Al<sub>2</sub>O<sub>3</sub> catalysts was also stated by other scientists, e.g. by Persson and her co-workers [12,13].

### 3.2. Catalyst activity

In Fig. 3 are shown the results of methane combustion on the catalyst (Pd–Pt/Al<sub>2</sub>O<sub>3</sub>) and on the support (Al<sub>2</sub>O<sub>3</sub>), and also in the empty reactor. The analyzed catalyst allows the initiation of the process of complete methane oxidation at the temperature about 600 K, while fifty percent of methane conversion can be obtained at about 750 K. At the temperature higher than 850 K, the reaction of methane combustion begins to run in the gas phase (without catalyst). The transient decrease in the catalyst activity observed at above 900 K is likely connected with the transformation of the oxidized phase of the palladium–platinum catalyst into the reduced phase. The oxidized phase of the Pd–Pt/Al<sub>2</sub>O<sub>3</sub> catalyst is probably more active than the reduced phase. Such behaviour was often observed, especially for palladium catalysts [26,27].

### 3.3. SSITKA results

The delay between argon and <sup>12</sup>CH<sub>4</sub> (or krypton and <sup>13</sup>CH<sub>4</sub>) demonstrates reversible adsorption of methane on the surface of the studied catalyst (Fig. 4). It proves that methane may be reversibly adsorbed except its irreversible adsorption (e.g. CH<sub>4</sub>-s + s → CH<sub>x</sub>-s + H-s; where s is surface adsorption site) leading to the oxidation products. That small delay (see inserted enlargement of the curves in Fig. 4) allows us to estimate the average surface life-time and the surface concentration of reversibly adsorbed

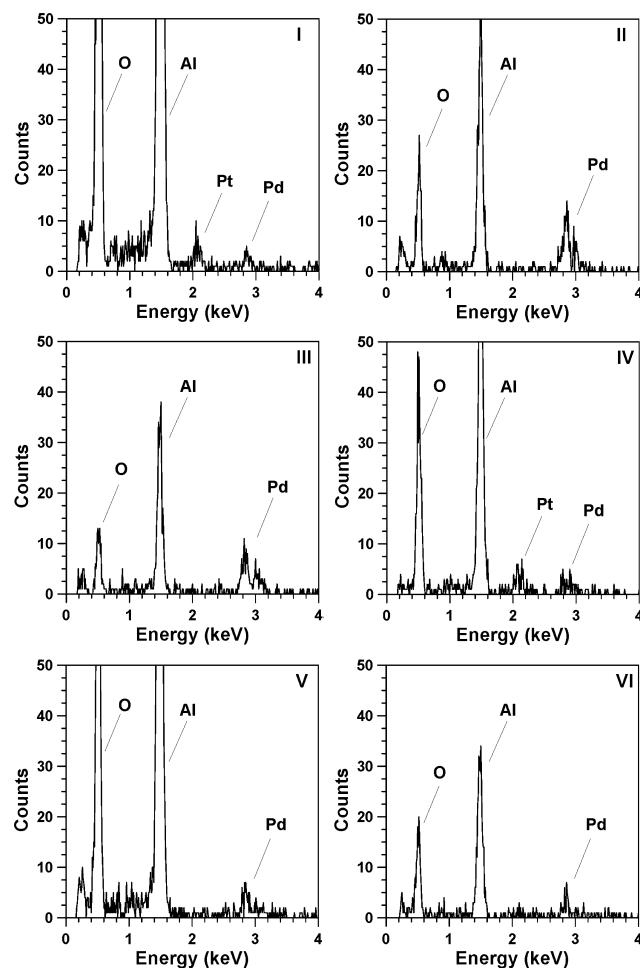


Fig. 2. Composition of active phase crystallites determined by the EDS spectroscopy.

molecules of methane and the number of adsorption sites used for that purpose (uncertainty of these measurements is determined by accuracy of the MS system). The reversible adsorption of methane we also observed in the process of complete methane oxidation on palladium catalysts [20,21].

The delays between argon and <sup>16</sup>O<sub>2</sub> (or krypton and <sup>18</sup>O<sub>2</sub>) demonstrate that oxygen adsorbs on the catalyst surface (Fig. 5). On

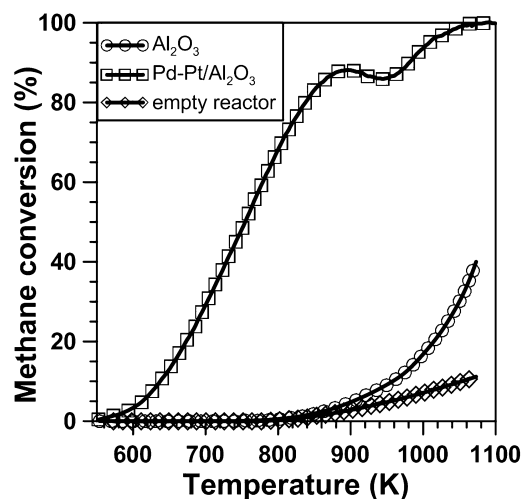


Fig. 3. Activity of the palladium–platinum catalyst in the process of complete methane oxidation.



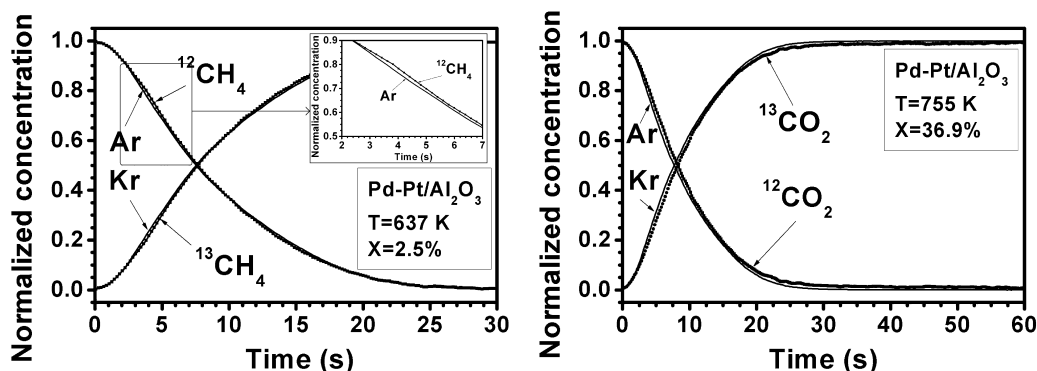


Fig. 4. Effect of the isotopic switching between  $^{12}\text{CH}_4/\text{Ar}/\text{O}_2/\text{He}$  and  $^{13}\text{CH}_4/\text{Kr}/\text{O}_2/\text{He}$  (X is the conversion of methane).

the base of these delays we can calculate the average surface life-time and the surface concentration of adsorbed oxygen, of course, assuming that there is no exchange between oxygen from the gas phase and oxygen from the crystal lattice of the catalyst. However, the presence of small amounts of oxygen molecules with different isotopes ( $^{16}\text{O}^{18}\text{O}$ ) and very slow disappearing of the signal coming from  $^{16}\text{O}_2$  after the isotope switching prove that oxygen from the gas phase not only adsorbs on the catalyst surface and takes part in the process of methane oxidation but also is exchanged with oxygen from the crystal lattice of the catalyst. The oxygen exchange was also observed, among others, by Ojala and his collaborators [28], as well as in our earlier studies [20,22] concerning methane oxidation over palladium catalysts.

The delays between argon and  $^{12}\text{CO}_2$  (or krypton and  $^{13}\text{CO}_2$ ) demonstrate the presence of carbon dioxide and the methane oxidation intermediates leading to formation of carbon dioxide, i.e. C-path of methane oxidation (Fig. 4) on the catalyst surface, and they can be also used for the calculation of the average surface life-time and the surface concentration of these molecules. The results of the isotopic switching from  $^{16}\text{O}_2$  to  $^{18}\text{O}_2$  (Fig. 5) provide information on O-path of  $\text{CH}_4/\text{O}_2$  catalytic reaction; not only about the average surface life-time and the surface concentration of carbon dioxide but also about the participation of oxygen from the crystal lattice of the catalyst in the process of complete methane oxidation. The latter is confirmed by the presence of significant amounts of  $\text{C}^{16}\text{O}^{18}\text{O}$  and very long delay between argon and  $\text{C}^{16}\text{O}_2$ . Similar behaviour was also observed for palladium catalysts [20,22]. Furthermore, the participation of oxygen from the crystal lattice of the catalyst indicates that the process of complete methane oxidation proceeds, at least partly, according to the Mars van-Krevelen mechanism. The similar conclusions were drawn, among others, by Ciuparu and Pfefferle [15] or Müller and his co-workers [17].

### 3.3.1. Average surface life-time and surface concentration

The obtained values of the average surface life-time and the surface concentration of  $^{12}\text{CH}_4$  show (left parts of Figs. 6 and 7—so-called “C-pool”) that methane molecules, reversibly adsorbed on the catalyst surface, are observed only at low temperatures, when the conversion of methane was a few percent. At higher temperatures, all adsorbed methane molecules are oxidized into carbon dioxide. It means that the sites on the catalyst surface that were not active in the process of complete methane oxidation become active with the temperature rise.

The values of the average surface life-time and the surface concentration of  $^{12}\text{CO}_2$  were divided on two parts (Figs. 6 and 7), because the delays between argon and  $^{12}\text{CO}_2$  (reaction product) consist of two maxima (Fig. 8). For comparison, such phenomenon was not observed in the case of the delays between argon and just reversibly adsorbed, not reacted  $^{12}\text{CH}_4$ . Of course, the precise estimation of these values is a big challenge, because the delays between Ar and  $^{12}\text{CO}_2$  are very short and observed maxima are strongly overlapped. Nonetheless, it is possible to distinguish them, which was also shown in our previous studies [20,21] concerning methane oxidation on palladium catalysts. Moreover, such results are rather common for the SSITKA studies [29–31] and prove that on the catalyst surface two different kinds of active centres are present. Since the inverse of the average surface life-time of  $^{12}\text{CO}_2$  can be treated as the reaction rate [18] and the surface concentration of  $^{12}\text{CO}_2$  corresponds to the concentration of active centres on the surface of the catalyst, we can state that on the surface of the palladium–platinum catalyst are more active but less numerous  $\alpha$  sites and less active but more numerous  $\beta$  sites. Moreover, the number of active centres on the catalyst surface is not stable but depends on the reaction conditions. Thus, the number of active centres determined on the basis of SSITKA studies is much

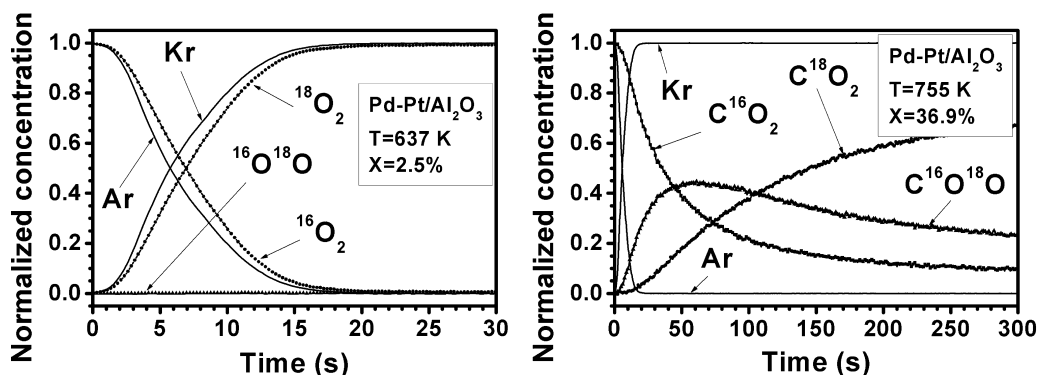
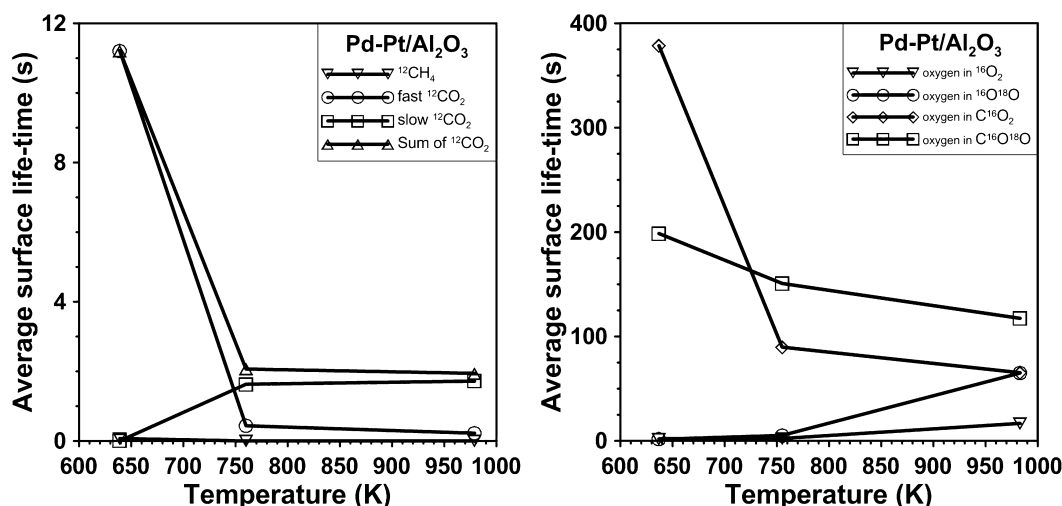


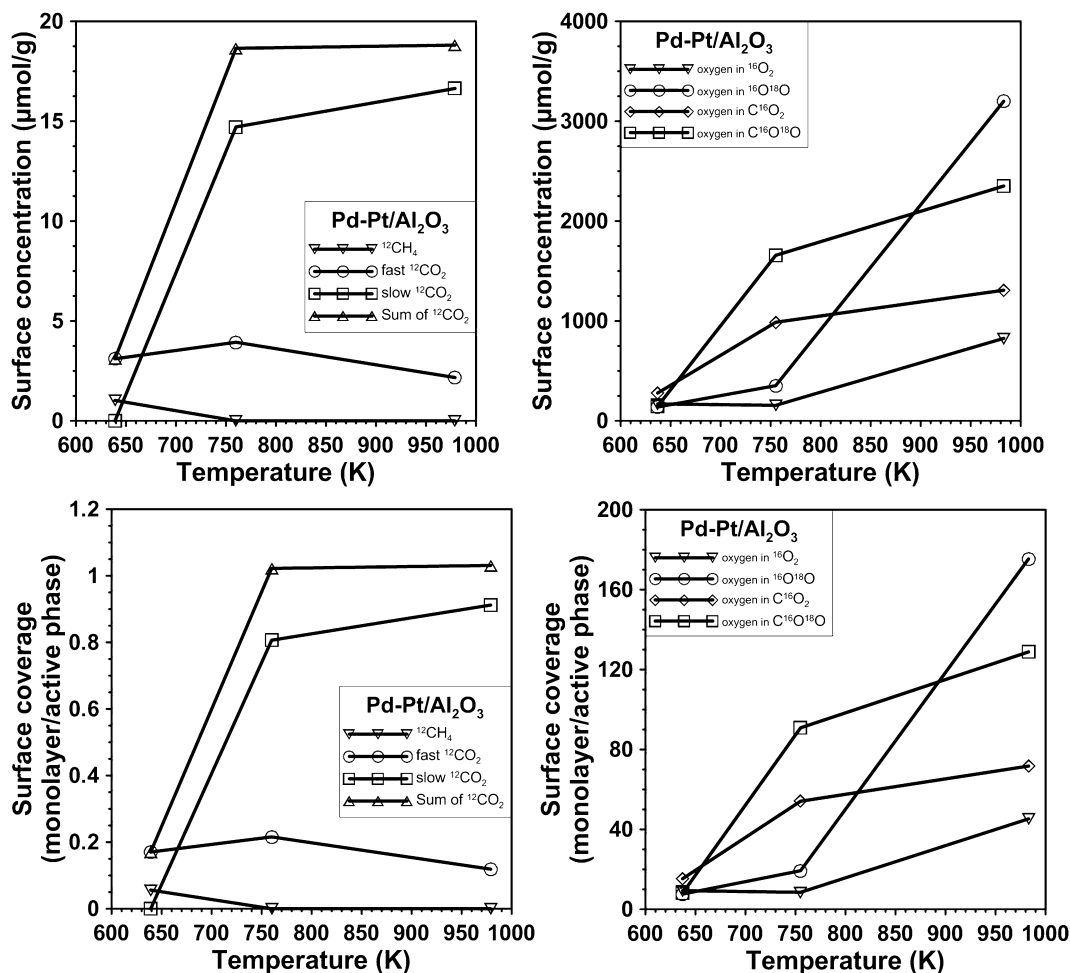
Fig. 5. Effect of the isotopic switching between  $^{16}\text{O}_2/\text{Ar}/\text{CH}_4/\text{He}$  and  $^{18}\text{O}_2/\text{Kr}/\text{CH}_4/\text{He}$  (X is the conversion of methane).



**Fig. 6.** Average surface life-time of methane, oxygen, carbon dioxide and methane oxidation intermediates leading to the formation of carbon dioxide (formed with fast and slow rates).

more close to the real values than their values obtained using the chemisorption of probe molecules under conditions far more different than those during methane oxidation. On the other hand, this method has also a few disadvantages. Certain problems can

be connected with the possible occurrence of such phenomena as: readsorption of CO<sub>2</sub> and formation of long-residing intermediates i.e. formates and carbonates. The presence of formates and carbonates was indicated by DRIFTS studies [32], while the readsorption



**Fig. 7.** Surface concentration of methane, oxygen, carbon dioxide and methane oxidation intermediates leading to the formation of carbon dioxide (formed with fast and slow rates), as well as the comparison of their values with the number of palladium and platinum atoms contained in the outer layer of the active phase of the Pd-Pt/Al<sub>2</sub>O<sub>3</sub> catalyst (surface coverage).

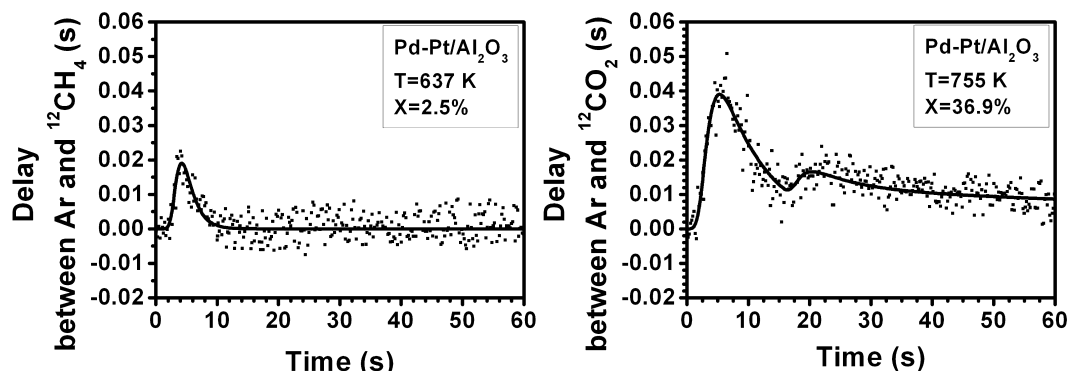


Fig. 8. Analysis of the delay between Ar and  $^{12}\text{CO}_2$  and also between Ar and  $^{12}\text{CH}_4$  (X is the conversion of methane).

of  $\text{CO}_2$  was observed for such process as the water gas shift reaction [23–25]. In our opinion, all these phenomena are possible, but the accuracy of estimation of their impact on the obtained values is almost impossible from our data. The higher surface concentration of carbon dioxide at higher than that at lower temperatures may support small contribution of adsorption of that reaction product to the whole amounts of carbon dioxide present on the catalysts surface. The opposite trend of the surface concentration changes with the raised temperature should be observed if the readsorption of carbon dioxide would be significant. The low partial pressure of carbon dioxide in our studies also does not encourage its significant adsorption. There are not numerous papers on adsorption of carbon dioxide on alumina at high temperatures. However, it was shown that it may be relatively high only on alumina surface chemically modified with alkaline metal or alkaline earth metal oxides or compounds [34]. The lower, left part of Fig. 7 shows that the formal coverage of the surface of metal phase with all C-containing species is only slightly over the monolayer at 750 K and above. It might lead to conclusion that overestimation of the C-pool is minor. However, it is very low probable that the active size necessary for oxidation of methane consists of only one surface metal atom. Therefore, we have to assume that the C-pool is overestimated. The extent of overestimation is still uncertain. As the activity of alumina support itself in the oxidation of methane is negligible up to 800 K and very low above that temperature of the process (see Fig. 3), participation of boundaries metal active phase-support in the reaction is the most likely and the carbon-containing intermediates ( $\text{CH}_4$ -s,  $\text{CH}_x$ -s,  $\text{CO}$ -s,  $\text{CO}_2$ -s) may reside also on the alumina support near to those boundaries.

Moreover, we are convinced that the readsorption of  $\text{CO}_2$  phenomena may influence, if any, rather only the number of  $\beta$  sites or the existence of  $\beta$  sites is caused by them. The SSITKA results do not supply almost any information about the composition of active centres. On the basis of STEM and EDS results it can be stated that the existence of two different active centres is connected with the existence of two different phases, but under reaction conditions, the phase composition of the Pd–Pt/ $\text{Al}_2\text{O}_3$  is different than after reduction, what was observed, among others, by Persson et al. [12,13]. Moreover, we also observed the existence of two different active centres for monometallic palladium catalysts [20,21]. At this point, we can also mention other hypothesis: more active  $\alpha$  sites can be referred to all kinds of edges, corners and defects of the catalyst lattice, the phase boundary between metal and oxide, whilst less active  $\beta$  sites—to flat surfaces, ideal terraces on palladium or platinum oxide or metal surface or metal-support boundaries, which become active only at higher temperatures.

The discussion on the topic concerning the origin of  $\alpha$  and  $\beta$  sites is very complex and without unequivocal information we have to leave this matter open, because there were some grounds for suggesting even more controversial opinions, e.g. the reaction of

methane oxidation is accompanied by the water gas shift reaction, as it was proposed in our earlier paper [21]. However, this paper, where not only  $^{12}\text{CH}_4/^{13}\text{CH}_4$ , as in the paper [21], but also  $^{16}\text{O}_2/^{18}\text{O}_2$  switches were employed, enables us to exclude in great probability that previous hypothesis.

The values of the average surface life-time of  $^{16}\text{O}_2$  and  $^{16}\text{O}^{18}\text{O}$  (right part of Fig. 6) refer to the life-time of oxygen on the surface of the catalyst and to the time necessary to exchange oxygen in the crystal lattice of the catalyst, while the obtained values of the surface concentration of  $^{16}\text{O}_2$  and  $^{16}\text{O}^{18}\text{O}$  (upper, right part of Fig. 7) refer to the oxygen concentration on the surface of the catalyst and to the concentration of oxygen in the crystal lattice of the catalyst that is being exchanged. Generally, all values of these kinetic parameters increase with the temperature rise. It means that the amount of oxygen which can be exchanged between the gas phase and the crystal lattice of the catalyst increase with the temperature rise. This fact is also confirmed by the increase of the average surface life-time of oxygen. Otherwise, its values should be decreased with the temperature rise like for methane molecules. Furthermore, at this point it should be noted that above 850 K oxygen can be also exchanged between the gas phase and the support lattice— $\gamma\text{-Al}_2\text{O}_3$ , as it was shown in [33].

The values of the average surface life-time of  $\text{C}^{16}\text{O}_2$  and  $\text{C}^{16}\text{O}^{18}\text{O}$  (right part of Fig. 6; so-called “O-pool”) refer to the average surface life-time of oxygen leading to formation of carbon dioxide and to the time necessary for exhaustion of the “old” oxygen ions in the catalyst lattice which may create  $\text{C}^{16}\text{O}_2$  and  $\text{C}^{16}\text{O}^{18}\text{O}$  molecules. The values of the surface concentration of oxygen leading to formation of  $\text{C}^{16}\text{O}_2$  and  $\text{C}^{16}\text{O}^{18}\text{O}$  (right part of Fig. 7; so-called “O-pool”)

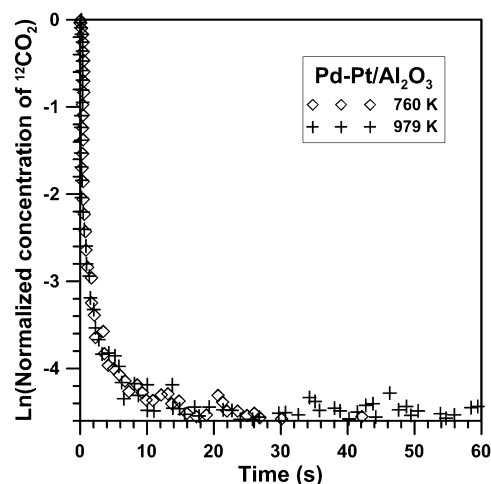


Fig. 9. Logarithmic analysis of the effects of the isotopic switching between  $^{12}\text{CH}_4/\text{Ar}/\text{O}_2/\text{He}$  and  $^{13}\text{CH}_4/\text{Kr}/\text{O}_2/\text{He}$ .

refer to the surface concentration of oxygen leading to formation of carbon dioxide and to the concentration of “old” oxygen ions in the catalyst lattice which may create  $C^{16}O_2$  and  $C^{16}O^{18}O$  molecules. Moreover, the possible exchange of oxygen atoms in carbon dioxide molecules can also influence the values of the average surface life-time and surface concentration of  $C^{16}O^{18}O$  and  $^{16}O^{18}O$  but not of the total concentration of active “O-pool”, the latter measured after integration of the  $C^{18}O_2$  and  $C^{16}O^{18}O$  transient response curves. The decrease of the values of the average surface life-time of  $C^{16}O_2$  and  $C^{16}O^{18}O$  suggests that the reaction rate of complete methane oxidation increases with the temperature rise. It is not depended on the kind of oxygen on the catalyst surface. This oxygen may derive from both the crystal lattice of the catalyst and from its surface as previously adsorbed from the gas phase. Moreover, the faster increase of the surface concentration of oxygen leading to formation of  $C^{16}O^{18}O$  in comparison to the concentration of oxygen leading to formation of  $C^{16}O_2$  suggests that the participation of oxygen from the crystal lattice of the catalyst in the process of complete methane oxidation is larger when the temperature is higher. In the lower, right part of Fig. 7, it is shown the formal coverage of the surface of palladium–platinum active phase with oxygen desorbed to the gas phase and oxygen leading to formation of carbon dioxide. This Figure clearly proves that a very large pool of subsurface oxygen participates in methane oxidation.

### 3.3.2. Mechanism of complete methane oxidation

Figs. 9 and 10 illustrate the effects of the so-called logarithmic analysis of the SSITKA results for the switching from  $^{12}CH_4$  to  $^{13}CH_4$  and for the switching from  $^{16}O_2$  to  $^{18}O_2$ . In both cases, at the beginning of the curve a small convexity is observed, while in the further part of chart a more visible concavity is seen. It suggests that, accordingly with SSITKA theory [18], the model of the surface of the palladium–platinum catalyst consists of pools in parallel and pools in series. The model of pools in series suggests that more than one intermediate between methane and carbon dioxide is present on the catalyst surface (Fig. 11). The existence of only one intermediate is rather impossible, because it would mean that during oxidation of the methane molecule all hydrogen atoms would be broken away in the same time and also in this moment two oxygen atoms would be bonded with carbon. The model of pools in parallel for the isotopic switching between  $^{12}CH_4$  and  $^{13}CH_4$  confirms information about the existence on the catalyst surface two different kind of active centres. On the other hand, the model of pools in parallel for the

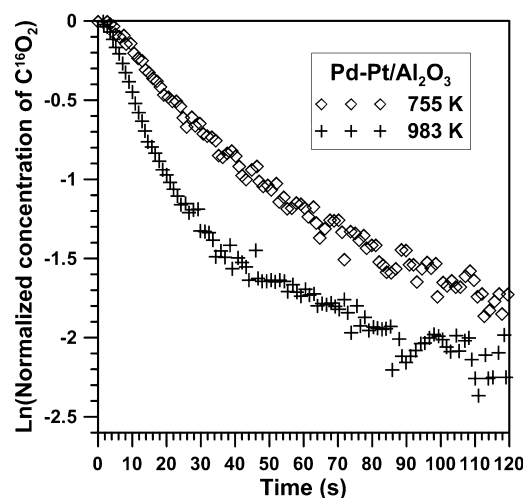


Fig. 10. Logarithmic analysis of the effects of the isotopic switching between  $^{16}O_2/Ar/CH_4/He$  and  $^{18}O_2/Kr/CH_4/He$ .

isotopic switching between  $^{16}O_2$  to  $^{18}O_2$  suggests the participation of two different kinds of oxygen atoms/molecules in the process of methane oxidation. It means that the process of complete methane oxidation on the palladium–platinum catalyst probably proceeds simultaneously according to two different kinds of the reaction mechanism. In the case of oxygen coming from the crystal lattice of the catalyst it is the Mars–van Krevelen mechanism, while for oxygen adsorbed from the gas phase it is the Langmuir–Hinshelwood mechanism. A similar proposal can be found in Müller and his co-workers' studies [17] and also in ours [20,21] concerning the reaction mechanism of methane oxidation both on palladium catalysts. Moreover, the process of methane oxidation proceeds not only simultaneously according to two different kinds of the reaction mechanism, but also with the different rates determined by the kind of active centres. It means that, the oxidation of methane on the  $\alpha$  sites proceeds simultaneously according to the Mars–van Krevelen mechanism and the Langmuir–Hinshelwood mechanism as well as the oxidation of methane on  $\beta$  sites also proceeds simultaneously by these two mechanisms. However, this hypothesis is also depended on the real nature/composition of these two kinds of active centres, which is unknown. The SSITKA method is not able to supply information on this topic and it is difficult to find today

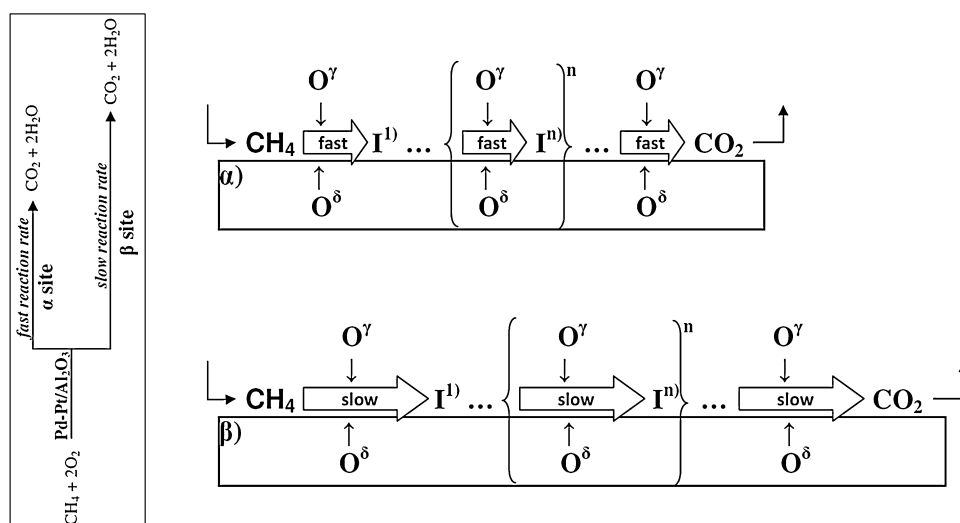


Fig. 11. Proposed scheme of complete methane oxidation on the palladium–platinum catalyst ( $\alpha$ ,  $\beta$ —active centres,  $O^\gamma$ —oxygen coming from the gas phase,  $O^\delta$ —oxygen coming from the crystal lattice of the catalyst,  $I^1$ ,  $I^n$ —intermediates of methane oxidation, where:  $n$ —their number).



any other method, which would be able to do it. Thus, the answer on this question we still have to leave open.

#### 4. Conclusions

Kinetic parameters as the average surface life-time and the surface concentration of methane, oxygen, carbon dioxide and intermediates leading to formation of carbon dioxide were determined in the steady state of methane oxidation over the  $\gamma$ -alumina palladium–platinum catalyst at temperatures 637, 755 and 980 K which enabled conversion of methane at low, medium and high level. It was found that carbon dioxide is formed with two different rates. On the basis of the  $^{12}\text{CH}_4/^{13}\text{CH}_4$  experiments we could determine the values of the average surface life-time of fast formed carbon dioxide which change from 11.2 s at 637 K to 0.2–0.3 s at higher temperatures, while the surface concentration of fast formed carbon dioxide and intermediates leading to it change from  $3.1 \mu\text{mol/g}$  at 637 K to  $1.8 \mu\text{mol/g}$  at 980 K. Carbon dioxide formed with a slow rate is present on the catalyst surface only above 637 K. At higher temperatures the values of its average surface life-time are close to 1.7–1.8 s, while the surface concentration of slow formed carbon dioxide and intermediates leading to it change from  $14.8 \mu\text{mol/g}$  at 755 K to  $16.3 \mu\text{mol/g}$  at 980 K. The coverage of the surface of the palladium–platinum active phase with fast formed carbon dioxide and intermediates leading to it is in the order of 0.16–0.17 in the range of 637–755 K and 0.125–at 980 K. Much more higher is the surface coverage with slow formed carbon dioxide –0.8 and 0.92 at 755 K and 980 K, respectively. Such large surface concentration of that kind of carbon dioxide and intermediates leading to it seems be probably a little overestimated—this question is still open. The very long live-time of oxygen leading to formation of carbon dioxide, in the order of 80–380 s, and very large formal coverage of the surface of palladium–platinum active phase with oxygen desorbed to the gas phase and oxygen leading to formation of carbon dioxide, scores of times exceeding the formal monolayer, clearly prove that a very large pool of subsurface oxygen participates in methane oxidation. It was also found that only at the lowest temperature a small amount of reversibly adsorbed methane resists in a very short life-time on the catalyst surface.

The presented results prove that the process of complete methane oxidation on the palladium–platinum catalyst proceeds simultaneously according to two different reaction mechanisms—the Mars–van Krevelen mechanism and the Langmuir–Hinshelwood mechanism. The extent of their participation in oxidation of methane molecules is different and depends on the reaction temperature. Moreover, two different kinds of active centres ( $\alpha$ —more reactive, but less numerous and  $\beta$ —less reactive, but more numerous) are present on the “working” surface of the catalyst. Their relative amounts also change with the temperature. The process of methane oxidation proceeds not only simultaneously according to two different reaction mechanisms, but also with the different rates determined by the kind of active centres. It means that oxidation of methane on  $\alpha$ -sites proceeds simultaneously according to Mars–van Krevelen and Langmuir–Hinshelwood mechanisms as well as oxidation of methane on  $\beta$ -sites also proceeds simultaneously by these two

mechanisms. Besides, the process of methane oxidation is accompanied by exchange of oxygen between the crystal lattice of the catalyst and the gas phase; this phenomenon also depends on the reaction temperature.

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